[TDCC Form Similar to: Form PTO-1390]

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER
44407

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known, see 37 C F R 1 5)
09/830507

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/US99/25974	**04 November 1999**	**05 November 1998**

TITLE OF INVENTION
NANOCOMPOSITE

APPLICANT(S) FOR DO/EO/US
Chai-Jing Chou; Eddy I. Garcia-Meitin

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [ ] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] has been transmitted by the International Bureau.
   c. [X] is not required, as the application was filed in the United States receiving Office (RO/US).
6. [ ] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [X] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [X] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the Annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 15. below concern other document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
13. [ ] A substitute specification.
14. [X] A change of power of attorney and/or address letter.
15. [ ] Other items or information:

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/830507	PCT/US99/25974	44407

17. [X] The following fees are submitted:		CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the EPO or JPO	$ 860.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482)	$ 690.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	$ 710.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445 (a)(2)) paid to USPTO	$ 1,000.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	$ 100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =		$ 860.00	
Surcharge of $ 130.00 for furnishing the oath or declaration later than ☐ 20 [X] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	+	$ 130.00	

Claims	Number Filed	Number Extra	Rate		
Total Claim	19 - 20 =	0	X $ 18.00	$ 0.00	
Independent Claims	4 - 3 =	1	X $ 80.00	$ 80.00	
Multiple dependent claim(s) (if applicable)			$ 270.00	$ 270.00	
Processing fee of $ 0 for furnishing the English Translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			+	$ 0.00	
			TOTAL NATIONAL FEE =	$ 1,340.00	
				Amount to be refunded:	$
				charged:	$

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.

b. [X] Please charge my Deposit Account No. **04-1512** in the amount of $ **1,340.00** to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **04-1512** . A duplicate copy of this sheet is enclosed.

Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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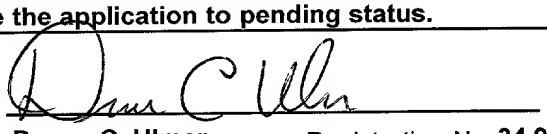
Signature: 

Duane C. Ulmer , Registration No. **34,941**

Date: **26 April 2001**

NANOCOMPOSITE

This invention relates to polymers reinforced with delaminated or exfoliated multi-layered silicates, that is, nanocomposite polymers.

Nanocomposite polymers are compositions comprising a relatively high number (but relatively low weight) of preferably single layers of exfoliated silicate material dispersed in a given volume of continuous polymer matrix, see United States Patent 5,717,000 to Seema V. Karande, Chai-Jing Chou, Jitka H. Solc and Kyung W. Suh, United States Patent Application Serial Number 034,620 filed December 31, 1996 and Giannelis, "Polymer Layered Silicate Nanocomposites", Advanced Materials, 1996, 8, No. 1, pages 29-35. As discussed in the '000 patent and as is well known in the art, nanocomposite polymers exhibit many increased physical property enhancements at a much lower weight percent of filler than conventionally filled polymers. Other patent literature disclosing nanocomposites include United States Patents 4,810,734, 4,556,075 and 3,516,959; as well as WO 93 04117 A and EP-A-0 459 472. Edge coating of multi-layer silicate material is known, see United States Patents 4,434,075 and 4,964,918.

However, it can be difficult to get the multi-layer silicate material to exfoliate into the polymer.

The instant invention is a solution, at least in part, to the above stated problem. In one embodiment, the instant invention is a process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoplastic polymer. The process comprises the step of mixing a quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer, characterized by the quaternary ammodium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material.

The instant invention in another embodiment is a process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoset polymer. The process of this embodiment comprises the steps of: (a) mixing a quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and (b) curing the thermoset prepolymer to set the thermoset polymer.

The instant invention in yet another embodiment is a composition comprising: (a) a polymer; and (b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, characterized by at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material.

The instant invention in further yet another embodiment is process for

producing a nanocomposite polymer, comprising the steps of: (a) mixing a quaternary ammonium intercalated multi-layered silicate material with a monomer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and (b) polymerizing the monomer.

Montmorillonite clay (a multi-layered silicate material) is stirred in water with an excess of 3,400 molecular weight sodium polyacrylate (a polyvalent anionic copolymer of mole ration 1:1 of ethylene and acrylic acid) available from the Rhone-Poulenc Company to edge treat the clay. The edge treated clay is then stirred with an excess of a mixed quaternary ammonium compound (68 percent bis hydroxyethyl, dodecyl, methyl-quaternary ammonium compound and 32 percent bis hydroxy C-6 to C-9, dodecyl, methyl-quaternary ammonium compound) to produce a polyacrylate edge coated quaternary ammonium intercalated montmorillonite. The polyacrylate edge coated quaternary ammonium intercalated montmorillonite is washed with water and dried. Ninety five parts of ethylene adipate thermoplastic polyurethane (available from The Dow Chemical Company) is melted (or softened) in a polymer mixer at 160 degrees Celsius at 200 rpm. Five parts of the dried polyacrylate edge coated quaternary ammonium intercalated montmorillonite, as described above in this paragraph, is added to the mixer and mixed for five minutes. Transmission light microscopic examination of the product shows significantly fewer one hundred micrometer sized clay clusters relative to the use of non-edge coated material. Transmission electron microscopic examination of the product shows single and multiple layer exfoliation of the silicate layers of the montmorillonite. The layers are counted in a representative view. Most preferably, more of the layers are present as single layers than are present as multiple layers. In any event the dispersion of the layers into the polymer is improved using the instant invention relative to the use of a non-edge-coated material.

Polyvalent anionic organic materials are organic chemicals that have more than one carboxylic acid or other anionic substituant such as a sulfonate or a phosphonate. Preferably the polyvalent anionic organic material is a polyvalent anionic polymer. Most preferably, the polyvalent anionic organic material is polyacrylic acid. However, the specific polyvalent anionic organic material used in the instant invention is not critical and can include, without limitation thereto, for example, copolymers of styrene and acrylic acid or styrene and sulfoethylmethacylate.

The above referred to '000 patent and the '620 patent application list exemplary multi-layered silicate materials required in the instant invention. For example, the multi-layered silicate material can be, without limitation thereto: montmorillonite; nontronite; beidellite; volkonskoite; hectorite saponite; sauconite; magadiite; medmontite; kenyaite;

laponite, mica, fluoromica and vermiculite. The above referred to '000 patent and '620 patent application also lists exemplary onium or quaternary ammonium compounds required in the instant invention. For example, the onium compound can be, without limitation thereto, quaternary ammonium compounds having octadecyl, hexadecyl, tetradecyl or dodecyl moieties. However, the specific multi-layered silicate material or onium compound used in the instant invention is not critical.

However, it should be understood that it is preferable to use polar substituted quaternary ammonium compounds with relatively polar polymers such as nylons and polyurethanes. Similarly, it is preferable to use non-polar substituted quaternary ammonium compounds with relatively non-polar polymers such as polypropylene and polyethylene. The terms "polar" and "non-polar" are used in their conventional sense. For example, a polar substituted quaternary ammonium compound is a quaternary ammonium compound having a hydroxy ethyl (C2OH) or hydroxy hexyl (C6OH) substituent(s) .

The selection of a preferred quaternary ammonium compound is aided by comparing the electron photomicrographs of the nanocomposites made using the quaternary ammonium compounds being tested in the instant invention to determine which quaternary ammonium compound(s) give the greatest degree of exfoliation of the multi-layered silicate. Of course, physical property improvement of the nanocomposite v. the base polymer is the final objective of the instant invention but such improvement is often a function of the degree of exfoliation of the multi-layered silicate.

In addition to mixing the polyvalent anionic organic quaternary ammonium intercalated multi-layered silicate material with a molten thermoplastic polymer, the instant invention also includes mixing the polyvalent anionic organic quaternary ammonium intercalated multi-layered silicate material with a monomer(s) or thermoset prepolymer(s) followed by the polymerization of the monomer(s)/prepolymer(s). Examples of thermoplastic polymers include, without limitation thereto, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers, urethane, epoxy, polyester, nylon, polycarbonate, and blends thereof. Examples of thermoset polymers include, without limitation thereto, epoxy, phenolic, urethane, rubber, and blends thereof.

1. A process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoplastic polymer, comprising the step of mixing a quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material.

2. The process of Claim 1, wherein the thermoplastic polymer is selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate; and blends thereof.

3. The process of Claim 1 or Claim 2, wherein the polyvalent anionic organic edge treated quaternary ammonium intercalated multi-layered silicate material exfoliates to produce single layers of silicate material and multiple layers of silicate material, the weight percent of the single layers of silicate material being greater than the weight percent of the multiple layers of silicate material as determined by transmission electron microscopy.

4. The process of Claim 1 or Claim 3, wherein the thermoplastic polymer is a blend of thermoplastic polymers.

5. A process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoset polymer, comprising the steps of:

(a) mixing a quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material;

(b) curing the thermoset prepolymer to set the thermoset polymer.

6. The process of Claim 5, wherein the thermoset polymer is selected from the group consisting of a thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.

7. The process of Claim 5 or Claim 6, wherein the polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material exfoliates in step (a) to produce single layers of silicate material and multiple layers of silicate material, the weight percent of the single layers of silicate material being greater than the weight percent of the multiple layers of silicate material as determined by transmission electron microscopy.

8. The process of Claim 5 or Claim 7, wherein the thermoset polymer is a blend of

thermoset polymers.

9. The process of Claim 1, wherein the thermoplastic polymer is selected from the group consisting of polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers and thermoplastic elastomers and blends thereof.

10. A composition comprising:

(a) a polymer; and

(b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, characterized by at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material.

11. The composition of Claim 10, wherein at least about one half of the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material.

12. The composition of Claim 10 or Claim 11, wherein the polymer is selected from the group of thermoplastic polymers and thermoset polymers and blends thereof.

13. The composition of Claim 12, wherein the thermoplastic polymers and thermoset polymers are selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers, thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.

14. The process of Claims 1-9, wherein the polyvalent anionic organic material is a polyacrylate.

15. The composition of Claims 10-13, wherein the polyvalent anionic organic material is a polyacrylate.

16. A process for producing a nanocomposite polymer, comprising the steps of:

(a) mixing a quaternary ammonium intercalated multi-layered silicate material with a monomer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and

(b) polymerizing the monomer.

17. The process of Claim 16, wherein the monomer is a blend of monomers.

18. The process of Claim 16, wherein the polymer is selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers,

thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.

19. The process of Claim 18, wherein the polyvalent anionic organic is a polyacrylate.

DECLARATION AND POWER OF ATTORNEY

USA/PCT

As a below named inventor, I hereby declare that:

(a) My residence and Citizenship are as stated below my name. My P.O. (mailing) address is the same as my residence unless otherwise stated.

(b) I verily believe I am/we are the original, first and sole/joint inventor(s) of the subject matter that is embraced by and for which a patent is sought on the invention entitled. **NANOCOMPOSITE**
and the specification of which: ☐ is attached hereto (_____).
(check one) ☒ was filed on November 04, 1999 as (44407).
Application No. PCT/US99/25974
and was amended on _____

(c) I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

(d) I acknowledge my duty under 37 CFR 1.56 to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56(b). If this application is a continuation-in-part application, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 CFR 1.56(b) that became available between the filing date of the prior application from which priority is claimed in part (f) below, and the national or PCT international filing date of this application.

(e) I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate listed below or §365(a) of any PCT international application that designated at least one country other than the United States of America listed below, and also identify below any other foreign equivalent application for patent or inventor's certificate or any other equivalent PCT international application having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)			PRIORITY CLAIMED	CERTIFIED COPIES INCL.
Number	**Country or PCT**	**Day/Month/Year Filed**		
_____	_____	_____	☐	☐

☐ Additional claims for benefit are attached.

(f) I hereby Claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below, or under 35 U.S.C. §120 of any United States application(s), or under § 365(c) of any PCT international application designating the United States of America listed below:

US or PCT Appln. Serial No.	Filing Date	Status at Application Filing Date
US Serial No. 60/108,979	November 18, 1998	Pending
US Serial No. 60/107,235	November 5, 1998	Pending

☐ Additional claims for benefit are attached.

I hereby appoint the attorney(s) and/or agent(s) at the following Customer No. to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith Address all correspondence to The Dow Chemical Company's appointed counsel at:

22515
PATENT TRADEMARK OFFICE

This appointment, including the right to delegate this appointment, shall also apply to the same extent it is applicable under the laws of the United States of America to any proceedings established by the Patent Cooperation Treaty.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

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At: _____
this ____ day of _____, 20____

Signature._____
Full Name:
Residence:

Country:
Citizenship:
P. O. Address:

At: _____
this _____ day of _____, 20____

Signature:_____
Full Name:
Residence:

Country:
Citizenship:
P. O. Address:

☐ Additional names and signatures are attached.